D46

STUDIES OF ATMOSPHERIC PHOTOCHEMISTRY AND KINETICS

Several laboratory measurement techniques have been developed at JPL for studying gas-phase chemical reactions which play important roles in atmospheric chemistry. These techniques have been designed to investigate the kinetic behavior of many different chemical species over a wide range of pressure and temperature. An important goal of the JPL Kinetics Laboratory is to study the reactions of these species under the same conditions of pressure, temperature, and humidity found in the atmosphere.

Interest remains high in the effect of emissions of halogen- and nitrogen-containing species on the vertical distributions of ozone and temperature in the stratosphere. These classes of compounds may, under certain conditions, participate in catalytic cycles that upset the natural formation and destruction processes of stratospheric ozone. Information is needed on the reactions that perturb this balance.

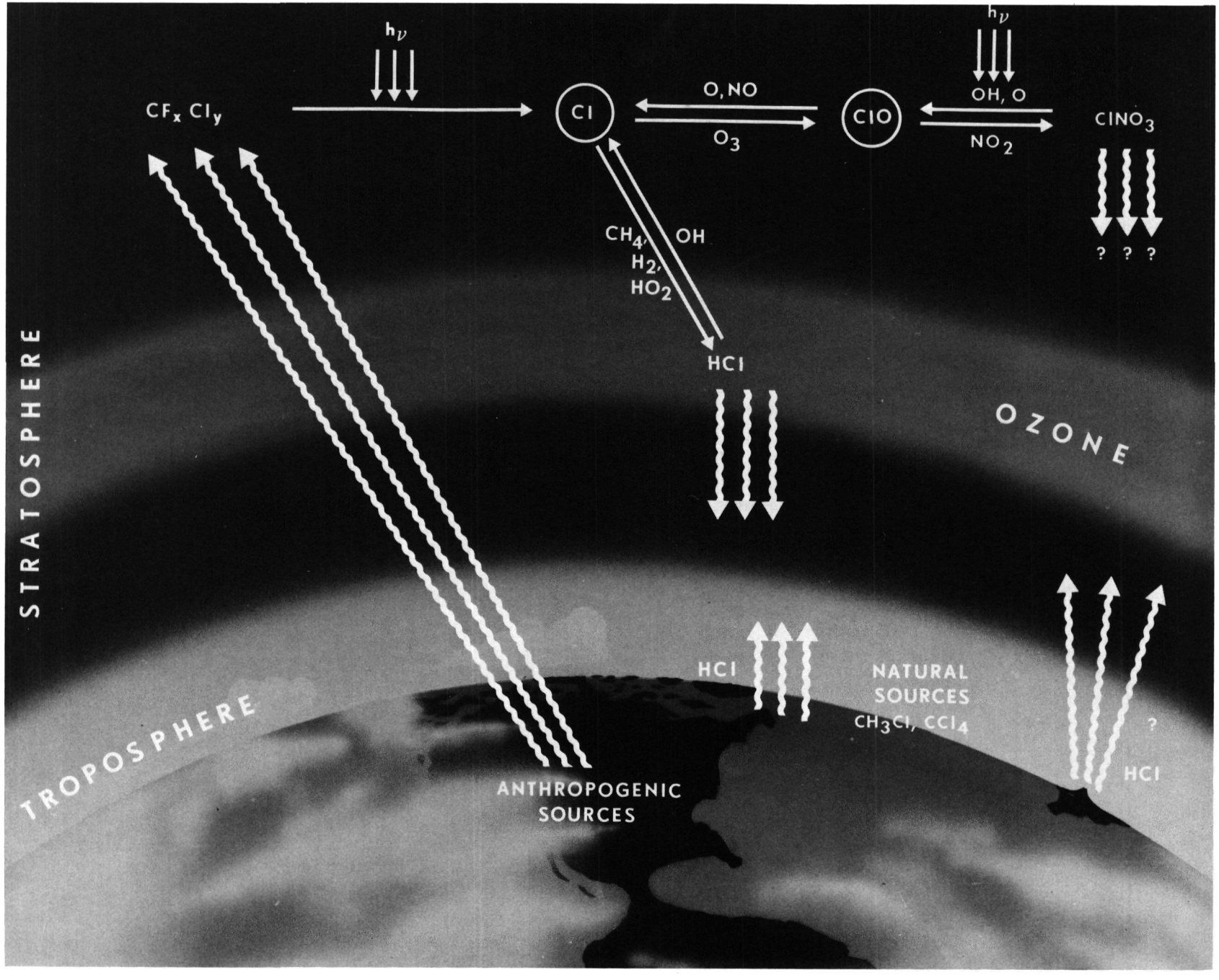
A concerted program at several NASA centers aims to understand the chemistry and transport of atmospheric gases in the unpolluted troposphere with a view toward evaluating the atmospheric impact of urban industrial sources. The chemistry of the lower atmosphere is influenced strongly by the reactions of the methane molecule, which is produced by a number of natural biological processes. When certain oxides of nitrogen are present, the methane oxidation cycle results in the formation of ozone. This process can be affected by industrial pollutants.

Major strides toward the understanding of the methane oxidation cycle were achieved at JPL by using a high-pressure flash-photolysis ultraviolet-absorption instrument. The first accurate measurements of the rate coefficient for the reaction of the elusive methylperoxy radical (an important species in the methane oxidation cycle) with nitrogen dioxide were made using this technique over a wide pressure range. The same apparatus was used to study the reactions of methylperoxy radicals with other trace atmospheric gases, including nitric oxide, sulfur dioxide, carbon monoxide, and other methylperoxy radicals.

Experiments with sulfur dioxide are particularly significant since it is the chemical transformation of this colorless gas into light-scattering aerosols that is responsible for visibility obscuring smog. The information gained was incorporated into complex models of chemistry and transport, which simulate the effects of pollutant emissions into the atmosphere.

The JPL laboratory also has contributed data on other atmospheric reactions involving the chlorine oxide, fluorine oxide, and hydroxyl radicals. A variety of state-of-the-art instruments has been developed using mass spectrometers, laser fluorescence systems, and other advanced detection devices.

Figure (opposite page): The drawing of Earth's atmosphere shows a highly simplified sequence of chemical reaction steps involving fluorocarbons that affect the stratospheric ozone layer. Research in the JPL Kinetics Laboratory is aimed at improving our understanding of the rates and mechanisms of these reactions. Among the important chemical species involved in stratospheric ozone (O_3) chemistry are chlorine compounds (Cl, ClO, $ClNO_3$, HCl), hydrogen (OH, HO_2, H_2O_2), and nitrogen (NO, NO_2, HNO_3) families as well as methane (CH_4), methyl chloride (CH_3Cl), and carbon tetrachloride (CCl_4). Other fluorocarbons are indicated by the chemical symbol CF_xCl_y.


hν
CFx Cly
Cl
O, NO
O3
ClO
hν
OH, O
NO2
ClNO3
? ? ?
CH4, H2, HO2
OH
HCl
STRATOSPHERE
OZONE
HCl
NATURAL SOURCES
CH3Cl, CCl4
?
HCl
TROPOSPHERE
ANTHROPOGENIC SOURCES